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学位授与の要件	課程博士(学位規則第4条第1項)
学位授与の題目	Low temperature magnetic properties of single crystal Van Vleck Paramagnets LiTmF ₄ and TmES (Van Vleck 常磁性単結晶 LiTmF ₄ 及び TmES の低温における磁気的性質の研究)
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Abstract. Lithium thulium fluoride LiTmF₄ is insulating Van Vleck paramagnet with the giant magnetostriction. Magnetization of the tetragonal LiTmF₄ single crystal was measured for the first time in the temperature range of 2–300 K and in the magnetic fields up to 55 kOe, oriented both parallel and perpendicular to the C₄ symmetry axis. Angular dependence of the magnetization in the basal plane was studied in particular. The anisotropy of magnetization in this plane was rapidly growing in high fields. Temperature dependence of the magnetization in the orientation $\vec{H} \parallel [001]$ is nonmonotonic and reproduced very well by the calculation in the framework of the crystal field theory. The results of calculation for the orientation $\vec{H} \perp [001]$ with taking into account the magnetostriction effects also agree well with the experimental data.

Susceptibility of single crystal Van Vleck paramagnet TmES was measured in the temperature range 2–300K and in magnetic fields up to 5.5 kOe in the orientation $\vec{H} \perp [001]$. Magnetic field dependence of susceptibility was measured for the first time. Rather fast decrease of susceptibility with the field increase is in agreement with the results of study of ¹⁶⁹Tm nuclear magnetic resonance spectra in TmES in recent works. TmES magnetic susceptibility is calculated with taking into account the effects of intermediate coupling.

1 Introduction

A special class of solid state magnetics — Van Vleck (VV) paramagnets — were subject for a study for a long time. Rather strong hyperfine interaction makes these compounds interesting for study of electron-nuclear magnetism. Magnetic field induced on the nucleus of the VV ion is many times larger than applied field. So, the frequencies of the nuclear magnetic resonance (NMR) in such compounds lay between usual NMR frequencies and the frequencies of the electron paramagnetic resonance (EPR). Therefore, one can say about so called "enhanced" NMR. Intermetallic VV paramagnets usually have cubic symmetry, while the majority of insulating VV paramagnets have the lower symmetry. Therefore, they are characterized by the anisotropy of magnetic susceptibility and effective gyromagnetic ratio of nuclei of VV ion ([1]).

From the point of view of the experimentalist, VV paramagnetism means that at high temperatures the magnetic susceptibility follows the Curie law, while at low temperatures it becomes constant. This behavior is explained by the absence of the magnetic moment of the ion in the ground state, i.e. the ground electronic state is either singlet or nonmagnetic doublet.

VV paramagnetism most frequently occurs in crystals, containing non-Kramers rare earth (RE) ions, i.e. RE ions with even number of electrons on unfilled $4f$ -shells (Pr^{3+} , Eu^{3+} , Tb^{3+} , Ho^{3+} , Tm^{3+}). Electrostatic crystal field (CF) lifts the degeneracy of the ground multiplet $^{2S+1}L_J$, and the typical Stark splittings are of the order of $10\text{-}100\text{ cm}^{-1}$. These splitting energy is much larger than the energy of the RE ion in the moderate magnetic fields. Therefore the Zeeman effect can be taken into account using the perturbation theory, and the VV paramagnetism appears in the second order of it.

Magnetic properties of the insulating VV paramagnets are studied rather well in the range of low temperatures and moderate magnetic fields, when the energies of the Zeeman interaction are much less than the energies of the Stark splittings. The main methods of study of these compounds in these conditions are magnetometry and enhanced NMR [1, 2, 3]. Further increasing of the magnetic field violates the applicability conditions for perturbation theory. It is difficult to say *a priori*, which effects will be displayed by these compounds in high magnetic fields.

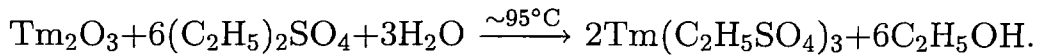
Polarized gaseous ^3He has the promising applications in medicine. One of the possible methods for achieving the high-polarized liquid ^3He state would be the transferring of the high-polarized state of magnetic moments in solid to the nuclear spins of liquid ^3He via magnetic coupling. Magnetically-anisotropic insulating VV paramagnets are rather promising compounds for study of magnetic coupling with nuclei of liquid ^3He . Strong anisotropy of NMR frequencies allows one to make the resonance frequencies of nuclear spins and liquid ^3He to coincide, and observe the resonance magnetic coupling. Magnetic coupling effects in such a compounds were observed in [4, 5] for the first time.

Present work covers the study of effect of high magnetic fields on magnetic properties of insulating VV paramagnets thulium ethyl sulfate $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (TmES) and thulium lithium fluoride LiTmF_4 .

2 Experimental details

LiTmF₄ crystal for investigation was grown by the Bridgman-Stockbarger method and was of a good optical quality. Samples for experiments were prepared from this grown crystal. Orientation along the symmetry axis [001] was controlled by the polarizing microscope, and the directions of [100] and [010] axes were found using the X-ray diffractometer. Axes [100] and [010] are indistinguishable. For the magnetization measurements the DC SQUID magnetometer MPMS by Quantum Design was used. It is designed to measure magnetic moments up to 1.25 emu. Preliminary measurements of LiTmF₄ in order to estimate the magnetic moment in maximal field suggested us to use a sample of about only 10 mg in weight then measuring M_{\perp} to avoid the exceeding of the instrument's range. It is difficult to preserve the orientation of such a small sample. Therefore it was decided to make the sample of the parallelepiped shape of $1.5 \times 1.5 \times 0.9$ mm in size. Larger face was normal to the symmetry axis [001] and was glued by epoxy resin to the flat bottom of the sample holder, which was oriented parallel to magnetic field. Increased area of the sample face which was glued to the sample holder, allowed to better preserve correct orientation $\vec{H} \perp [001]$. In order to keep sample free to change its size due to magnetostriction, only a small amount of epoxy resin was used. The shape of the sample leads to increase of the local field at Tm³⁺ ions in the orientation $\vec{H} \perp [001]$ by 2%. Experimental results were corrected by this value. In the measurements of the angular dependence of M_{\perp} , sample was rotated in (001) plane with an accuracy of $\pm 1^{\circ}$. Since at liquid helium temperatures susceptibility χ_{\parallel} is about 40 times smaller than χ_{\perp} , a cubic sample of much larger mass (about 400 mg) was used in experiments in the orientation $\vec{H} \parallel [001]$.

Raw materials for growing of the TmES crystals were thulium oxide (purity is 99.9%) and diethylsulfate (ethyl ester of sulfuric acid) (purity is 97%). The thulium ethylsulfate solution was obtained according to the following reaction:



TmES single crystals were grown by free evaporation of the saturated solution at room temperature in a glass cup with flat bottom. The growing speed was chosen by changing of effective evaporation area. TmES single crystals grew as hexagonal prisms with axes along crystallographic axis *c*. Side faces corresponded to *a* and *b* planes. To make the sample for measurement, the grown

crystal was filed to a spherical shape with preserving of its c axis orientation.

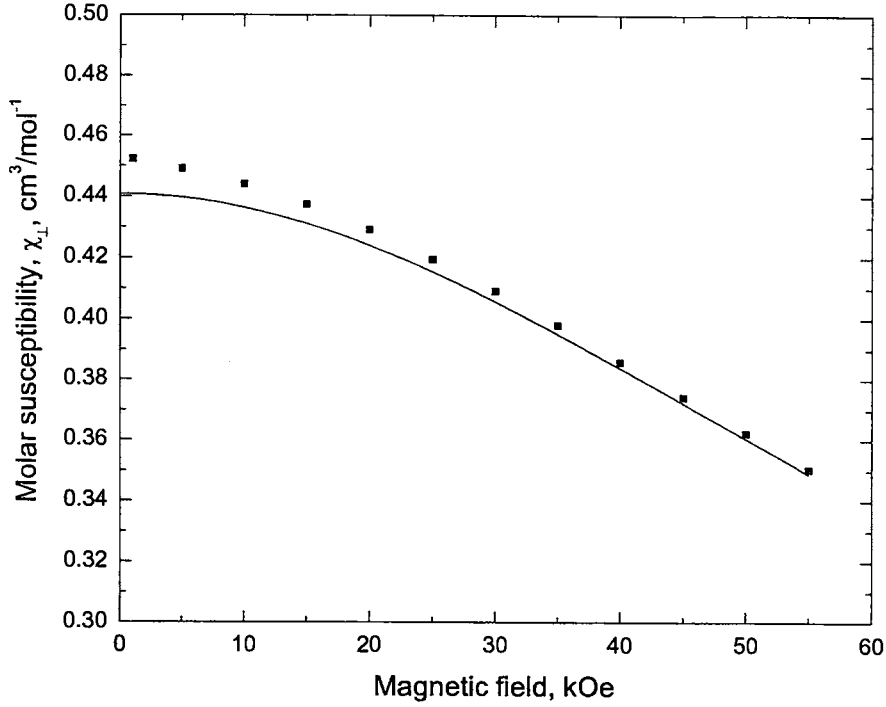


Figure 1: Magnetic field dependence of TmES susceptibility in the orientation $\vec{H} \perp [001]$. Temperature is 4.2 K. Symbols (\blacksquare): experimental data; line (—): result of calculation.

3 Results

3.1 TmES single crystal

The following dependences of TmES susceptibility were measured in the orientation $\vec{H} \perp [001]$:

- temperature dependence in the range of 2–300 K
- field dependence in the range of 1–55 kOe at temperature 4.2 K.

Magnetic field dependence is presented on Fig. 1. At temperatures of liquid helium in the orientation $\vec{H} \perp [001]$ the susceptibility is monotonically decreases.

Temperature dependence is presented on Fig. 2. In accordance with the results of calculations in the earlier work [6], the experiments on TmES in present work showed that magnetization below 8 K is temperature-independent. This is the distinctive feature of Van Vleck paramagnets.

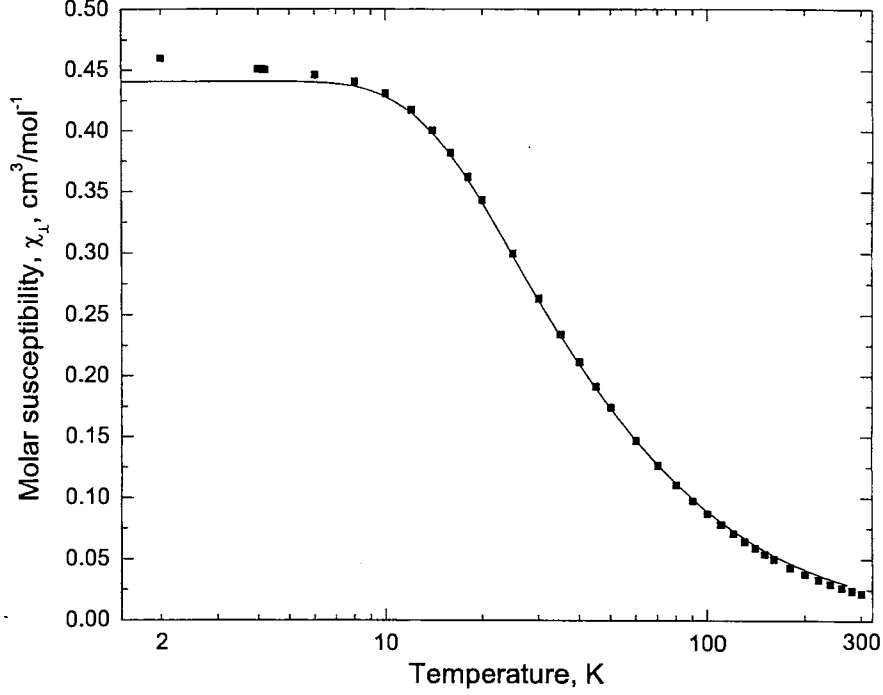


Figure 2: Temperature dependence of TmES susceptibility in the orientation $\vec{H} \perp [001]$. Magnetic field $H=1$ kOe. Symbols (\blacksquare): experimental data; line (—): result of calculation.

3.2 LiTmF₄ single crystal

The following dependences of LiTmF₄ magnetization were measured in the orientation $\vec{H} \perp [001]$:

- temperature dependences in the range of 2–300 K in two orientations of the sample in (001) plane
- field dependences in the range of 0.1–55 kOe in two orientations of the sample in (001) plane at temperature 4.2 K
- angular dependences in (001) plane at 4.2 K in strong and weak magnetic fields.

These measurements were performed using the small sample of 10 mg mass. Beside this, the temperature dependence in the range of 2–300 K in the orientation $\vec{H} \parallel [001]$ was measured with a larger sample of mass about 400 mg.

The angular dependences of magnetization M_{\perp} in various magnetic fields are presented on Fig. 3, where the magnetic field direction is defined by the angle

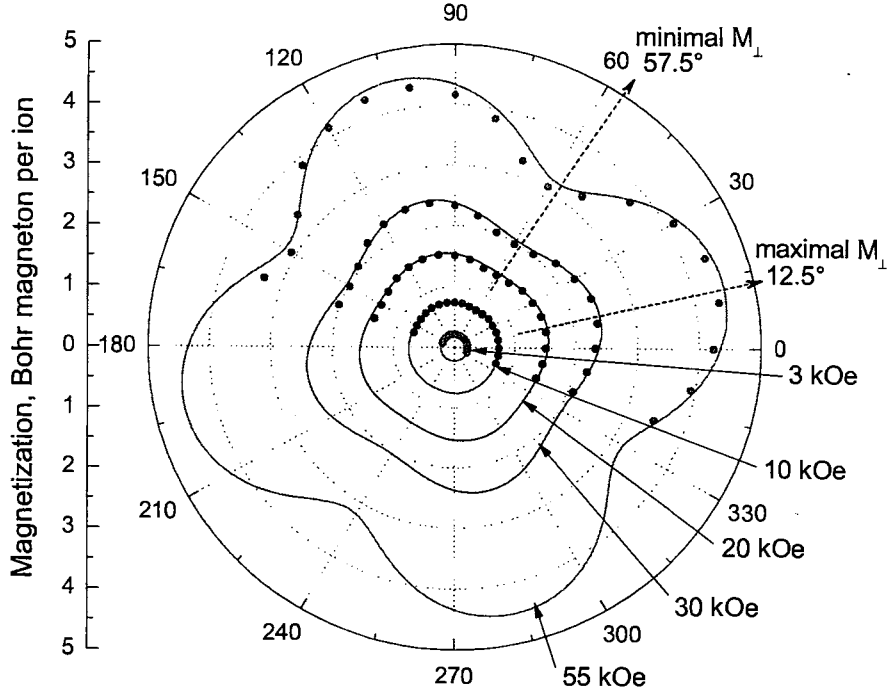


Figure 3: Angular dependences of LiTmF_4 magnetization at various magnetic fields $\vec{H} \perp [001]$. Temperature is 4.2 K. Symbols (\bullet): experimental data; lines (—): results of calculation. In all the cases the experimental points which are nearest to the calculated curve were obtained at the same field as this curve was calculated for.

φ , measured from the crystallographic axis $[100]$. Maximum magnetic field used was 55 kOe. One can see that magnetic anisotropy in (001) plane rapidly increases with magnetic field. Maximum and minimum of M_{\perp} are reached at angles $\varphi = \varphi_{\max} \approx 12.5^\circ + 90^\circ \cdot n$ and $\varphi = \varphi_{\min} \approx 57.5^\circ + 90^\circ \cdot n$, respectively.

The field dependences are presented on Fig. 4. At the temperatures of the liquid helium in the orientation $\vec{H} \perp [001]$, φ_{\max} the susceptibility is growing with field and the maximum is reached at field of about 43.5 kOe. While in the orientation $\vec{H} \perp [001]$, φ_{\min} it decreases monotonically. In this direction the crystal behaves as if there is no magnetostriction.

Experiments showed that in the orientation $\vec{H} \parallel [001]$ susceptibility is independent on magnetic field up to 55 kOe.

Temperature dependences were measured in three orientations: in (001) plane for $\varphi = \varphi_{\max}$ and $\varphi = \varphi_{\min}$; i.e. in the orientations of maximum and minimum susceptibility in this plane, and in the orientation $\vec{H} \parallel [001]$. In accordance

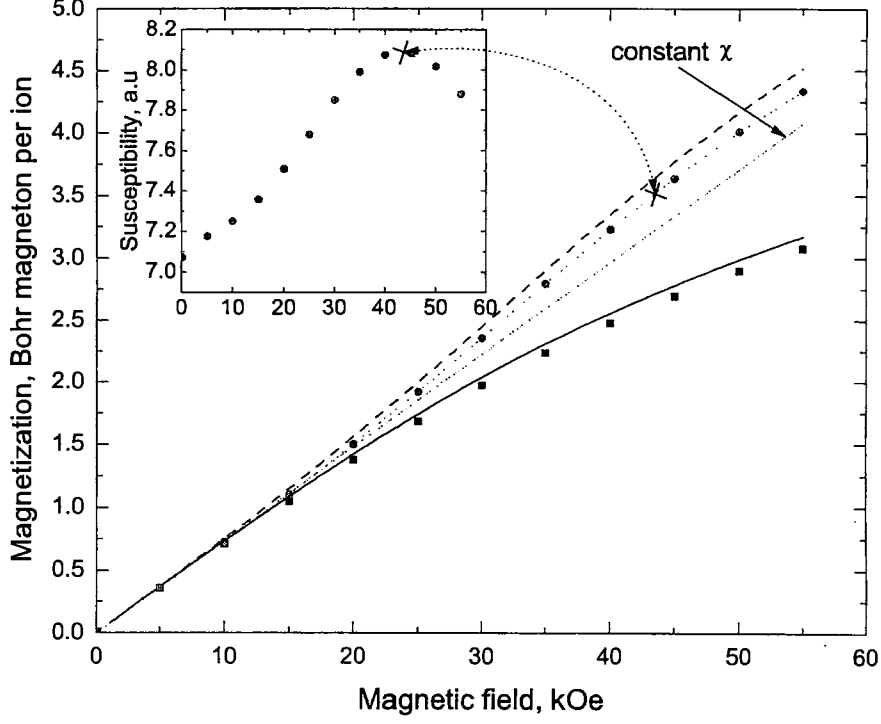


Figure 4: Magnetic field dependences of LiTmF_4 magnetization in the orientation $\vec{H} \perp [001]$. Temperature is 4.2 K. Symbols correspond to the experimental data; (\blacksquare): $\varphi = 57.5^\circ$; (\bullet): $\varphi = 12.5^\circ$. Lines are results of calculation; (—): $\varphi = 57.5^\circ$; (---): $\varphi = 12.5^\circ$. In the experiment the maximum susceptibility χ_\perp is reached at field ≈ 43.5 kOe for $\varphi = 12.5^\circ$ (shown on the inset).

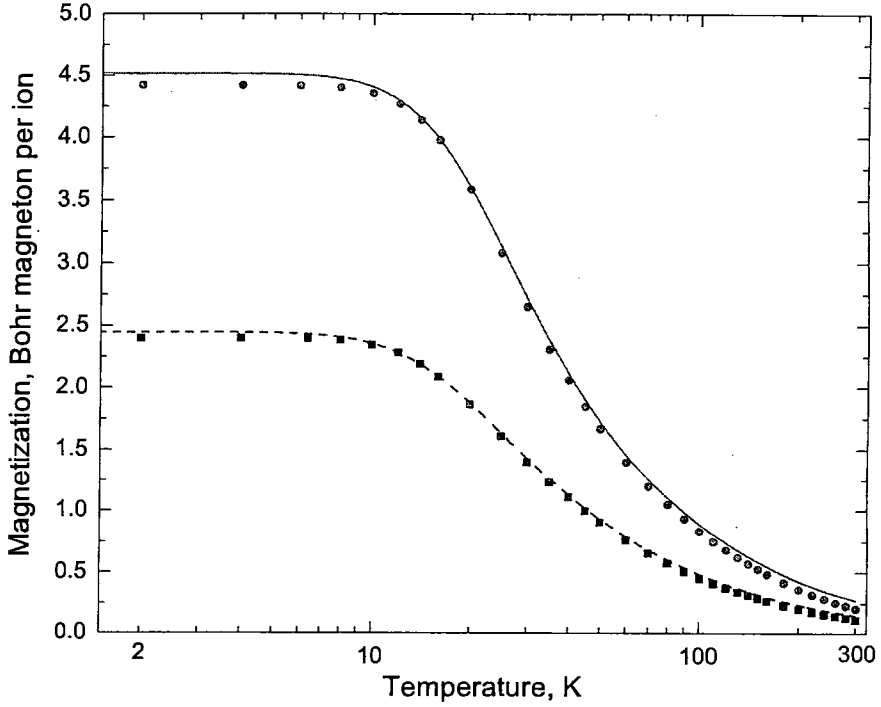


Figure 5: Temperature dependences of LiTmF_4 magnetization in the orientation

$\vec{H} \perp [001]$, $\varphi = 12.5^\circ$. Symbols correspond to experimental data; (\bullet): $H=55$ kOe; (\blacksquare): $H=30$ kOe. Lines are the results of the calculation; (—): $H=55$ kOe; (---): $H=30$ kOe.

with the results of calculations for dilute crystals ([7, 8]), the experiments on LiTmF_4 in present work showed that magnetization below 8 K is temperature-independent (Fig. 5 and 6). This temperature independence shows that there is only an insignificant amount of impurities, i.e. sources of conventional paramagnetism in the sample.

In the orientation $\vec{H} \parallel [001]$ temperature dependence of magnetization is nonmonotonic (Fig. 7). This is a frequently displayed feature of Van Vleck paramagnets in the orientation of the minimal susceptibility, since magnetic ions in the excited CF states usually have larger magnetic moments.

4 Conclusion

Susceptibility of the single crystal Van Vleck paramagnet TmES was measured in the temperature range 2–300K and in magnetic fields up to 5.5 kOe. Mag-

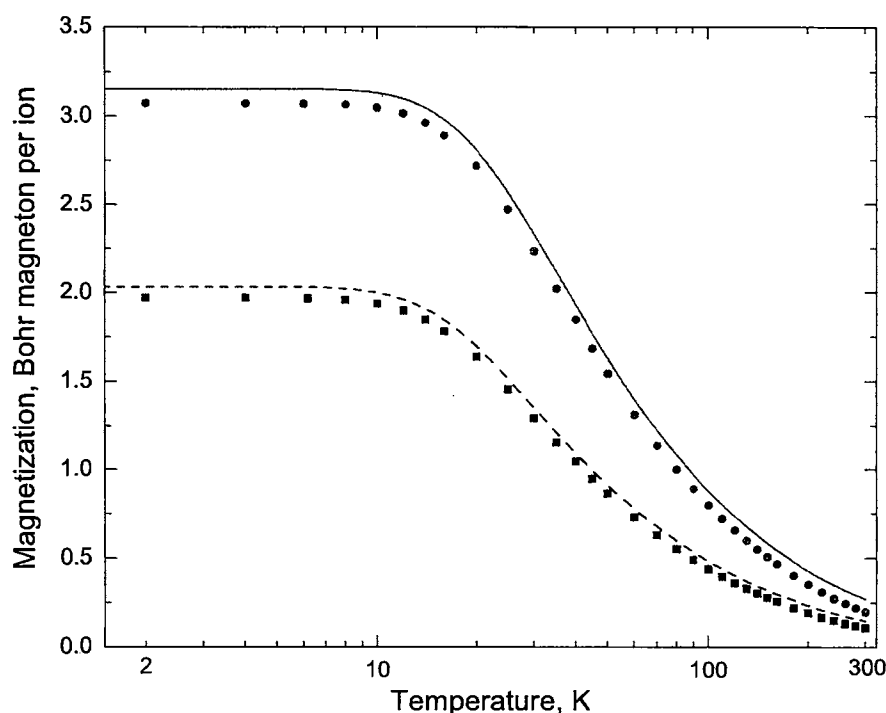


Figure 6: Temperature dependences of LiTmF_4 magnetization in the orientation $\vec{H} \perp [001]$, $\varphi = 57.5^\circ$. Symbols correspond to experimental data; (\bullet): $H=55$ kOe; (\blacksquare): $H=30$ kOe. Lines are the results of the calculation; (—): $H=55$ kOe; (---): $H=30$ kOe.

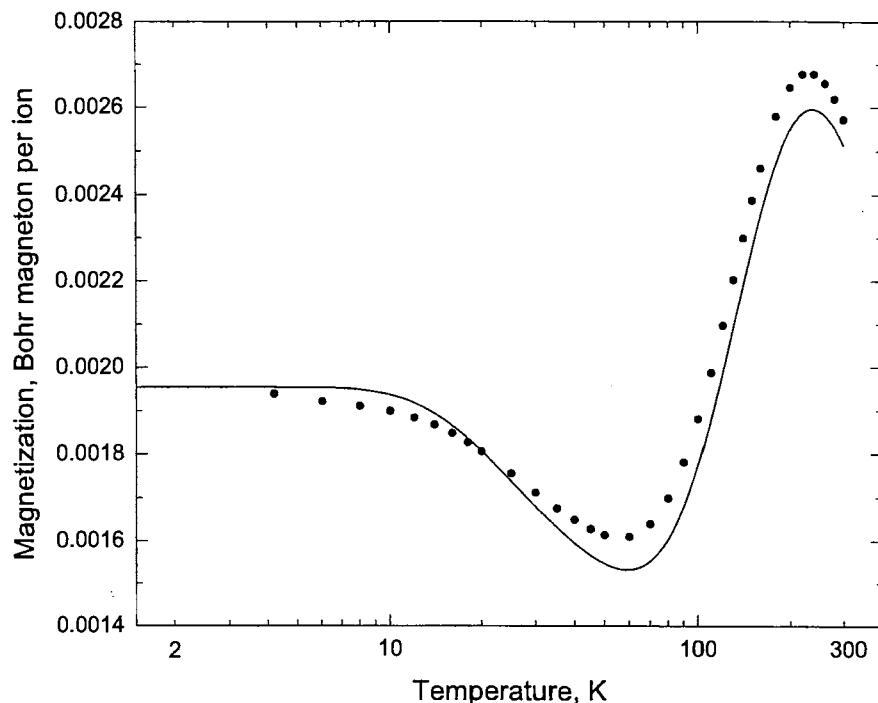


Figure 7: Temperature dependence of LiTmF_4 magnetization. $\vec{H} \parallel [001]$, $H=1$ kOe. Symbols (\bullet): experimental data; line (—): result of calculation.

netic field dependence of susceptibility was measured for the first time. Rather fast decrease of susceptibility with the field increase is in agreement with the results of study of ^{169}Tm NMR spectra in TmES in [9, 10]. TmES magnetic susceptibility is calculated with taking into account the effects of intermediate coupling. This allowed to improve the agreement between calculated and experimental temperature dependences of TmES susceptibility in comparison to the work [6].

Magnetization of the single crystal Van Vleck paramagnet LiTmF_4 was measured for the first time in the temperature range of 2–300 K and in the magnetic fields up to 55 kOe oriented both parallel and perpendicular to the C_4 symmetry axis. The anisotropy of the magnetization in the basal plane was rapidly growing in high fields, which is in agreement with the recent results of the measurements of the angular dependence of effective gyromagnetic ratio of ^{169}Tm nuclei in LiTmF_4 in high fields in work [11]. Temperature dependence of the magnetization in the orientation $\vec{H} \parallel [001]$ was nonmonotonic and reproduced very well by the calculation in the framework of the crystal field theory. The results of calculation for the orientation $\vec{H} \perp [001]$ with taking into account the magnetostriction effects also agree well with the experimental data.

Additionally, the crystal field parameters set for LiTmF_4 crystal was cor-

rected in this work in order to fit the positions of the maxima of the angular dependence of magnetization M_{\perp} to those of experimental data.

It is known as a remarkable feature of the Van Vleck paramagnets that NMR of nuclei of paramagnetic ions can be observed at low temperatures. NMR of ^{169}Tm can be used to probe the magnetic moment of $4f$ shell of Tm^{3+} ions in LiTmF_4 . In [12] it was found experimentally that the direction of the maximum effective gyromagnetic ratio of ^{169}Tm nuclei in LiTmF_4 crystal in (001) plane corresponds to the angle $\varphi \sim 11^\circ$ between the [100] axis and the magnetic field directions. This result is in good agreement with the value of $\varphi_{\max} = 12.5^\circ$ for the direction of the maximum magnetization determined in present work.

It is clear from the figure 4 that no structural phase transitions which affect LiTmF_4 magnetization occur in the used magnetic field range. This suggests us to propose that sharp jumps of the magnetization of the powder samples in [13] in the magnetic fields above 40 kOe occurred due to size effect.

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学位論文審査結果の要旨

Abubakirov Denis Irikovich 君の学位論文について、上記 5 名の審査委員による査読の後、平成 20 年 7 月 31 日に口頭発表が行われた。同日に審査会を開き、以下のように博士(学術)に値するものと判定した。

本論文は Van Vleck 常磁性体である TmES (thulium ethyl sulfate) と LiTmF_4 の単結晶について、磁化を精密に測定し、結晶場を考慮した詳細な解析を報告している。Abubakirov 君は TmES 単結晶を自ら作製し、2~300K の温度領域において 55kOe の磁場強度まで帯磁率を測定した。帯磁率の磁場強度依存性は本研究で初めて報告された。磁場強度増加に伴い帯磁率の減少を観測したが、これは ^{169}Tm の NMR 測定と一致した。帯磁率は、中間結合状態を考慮した解析で計算され、従来の解析より実験結果をよく説明できることを明らかにした。

LiTmF_4 単結晶については、 C_4 対称性軸に垂直と平行方向の帯磁率を、2~300K の温度範囲と 55kOe の磁場強度領域において、初めて報告した。 LiTmF_4 の底面内の磁化の異方性は磁場強度とともに急速に増加した。結晶の [001] 方向に平行な方向での磁化は温度とともに単調に変化したが、これは結晶場理論による解析によってよく説明できた。結晶の [001] 方向に垂直な方向の磁化測定結果に対する解析は、結晶の磁気歪みの効果を考慮することによって実験結果を良く再現することが出来た。

以上の研究結果により、本論文は学位に値する物と判断され、合格と判定された。